ELECTRONIC SPECTRA OF *m*-CHLOROPHENOL AND *o*-BROMOANISOLE IN DIFFERENT STATES*

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ABSTRACT. The ultraviolet absorption spectra of *m*-chlorophenol and *o*-bromoanisole in the vapour, liquid and solid states have been studied. In the vapour phase, *m*-chlorophenol yields about fifty sharp bands with the 0,0 band at 35761 cm^{-1}. The observed frequencies are 151, 190 and 235 cm^{-1} in the ground state and 120, 180, 225, 362, 503, 612, 737, 858, 959, 1029 and 1086 cm^{-1} in the excited state. In the spectrum of the liquid, the bands are broad and the 0,0 band is displaced by about 260 cm^{-1} towards red with respect to its position in the vapour phase. When the liquid is frozen and cooled to $-180°C$, no further change in the spectrum is observed.

In the spectrum of *o*-bromoanisole in the vapour state the 0,0 band is at 35615 cm^{-1} and the observed excited state frequencies are 221, 358, 517, 632, 685, 744, 955, 1031 and 1233 cm^{-1}. The bands observed in the spectrum of the liquid are broad and the 0,0 band is shifted by about 390 cm^{-1} towards longer wavelengths from its position in the spectrum of the vapour. With solidification of the liquid and cooling to $-180°C$, no appreciable change is observed in the spectrum.

INTRODUCTION

The ultraviolet absorption spectra of a large number of disubstituted benzene compounds in different states have been investigated in this laboratory to study the influence of intermolecular forces on the position and structure of absorption bands in the liquid and solid states. The present work is an extension of such investigations to the case of *m*-chlorophenol and *o*-bromoanisole.

It appeared that the ultraviolet absorption spectra of these compounds in any state had not been studied by any previous worker. The absorption spectra of the compounds in the vapour, liquid and solid states have, therefore, been analysed and the changes in the spectra observed with the change of state and temperature have been discussed in the present paper.

EXPERIMENTAL

The experimental set-up was the same as that described in an earlier paper (Banerjee, 1956). Chemically pure *m*-chlorophenol and *o*-bromoanisole obtained from Fisher Scientific Co., U.S.A., were used after fractional and

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repeated vacuum distillation. For studying the absorption spectrum in the vapour state, cells of length 50 cm and 20 cm respectively and provided with quartz windows and a bulb attached to a side tube for containing the liquid, were used. In order to obtain suitable pressure of the absorbing vapour, the temperature of the liquid was varied from $-20°C$ to $32°C$ by immersing the container in suitable low temperature baths while the absorption tube was kept at the room temperature (about $32°C$).

Thin films of the substances of thickness of the order of a few microns were required to produce bands in the liquid and solid states. The spectrograms were taken on Agfa Isopan films with a Hilger E 1 spectrograph giving a dispersion of about 3A per mm. in the 2600Å region. Microphotometric records were taken with a Kipp and Zonen type Moll microphotometer and the absorption spectra were calibrated with the help of microphotometric records of iron arc spectrum photographed on each spectrogram as explained in a previous paper (Banerjee, 1956).

RESULTS AND DISCUSSION

The microphotometric records of the absorption spectra of *m*-chlorophenol and *o*-bromoanisole are reproduced in Figs. 1, 2, 3 and 4. The wave numbers of the bands with their approximate visual intensities and probable assignments are given in Tables I, II, III and IV.

The near ultraviolet absorption system in the case of the molecules of both the compounds, belonging to C_s point group, is due to an allowed $A'-A'$ transition, with the transition moment lying in the plane of the molecule. Accordingly, the spectrum in each case consists of a number of intense bands with a strong 0, 0 band. The results obtained for the two compounds are discussed separately in the following paragraphs.

m-Chlorophenol

About fifty sharp bands have been recorded in the spectrum due to *m*-chlorophenol in the vapour state. The most intense band at 35761 cm^{-1} on the long wavelength side of the spectrum which persists at low pressure of the absorbing vapour has been taken as the 0, 0 band. The other bands may then be explained in terms of frequencies 151, 190 snd 235 cm^{-1} in the ground state and 120, 180, 225, 362, 503, 569, 612, 737, 858, 959, 1029 and 1086 cm^{-1} in the excited state. The Raman spectrum of the substance was studied by Kohlrausch and Pongratz (1935) who reported the frequency shifts, 193(3), 241(2b), 409(3), 527(1), 684(3), 769(0), 890(1), 995(6), 1066(3), 1088($\frac{1}{2}$), 1157(0), 1253(2b), 1304(0), 1583(3b) and 3070(0) cm^{-1}, the intensities being given in the parentheses. It can be seen that the frequencies observed in the present investigation can be correlated with the

TABLE I

Ultraviolet absorption bands of *m*-chlorophenol in the vapour state

Wave No. (cm^{-1}) and Intensity	Assignment	Wave No. (cm^{-1}) and Intensity	Assignment
35526 (m)	0−235	36988 (vw)	0+1227
			0+2×612
35572 (w)	0−190		
		37071 (w)	0+959+362
35610 (w)	0−151		
		37212 (vw)	0+858+612
35678 (m)	0−83		0+959+503
35710 (m)	0−235+180	37232 (vw)	0+2×737
35761 (s)	0,0	37316 (w)	0+1555
			0+959+612
35793 (w)	0+180−151		0+1029+503
35834 (m)	0+225−151	37386 (m)	0+1625
35881 (s)	0+120	37470 (m)	0+2×858
			0+959+737
35941 (m)	0+180		
		37568 (m)	0+959+858
35986 (m)	0+225		
		37604 (m)	0+1086+737
36123 (w)	0+362		0+3×612
36264 (w)	0+503	37670 (s)	0+2×959
36330 (w)	0+569	37700 (vw)	0+1086+858
36373 (m)	0+612	37736 (vw)	0+959+1029
36498 (m)	0+737	37810 (vw)	0+959+1086
			0+2×1029
36619 (m)	0+858		
		37856 (w)	0+1029+1086
36653 (m)	0+858+180−151		
		37949 (m)	0+2×1086
36672 (w)	0+858+225−151		
	0+959−235+180	37982 (m)	0+3×737
36720 (s)	0+959	38033 (m)	0+2×959+362
36753 (w)	0+959+180−151	38346 (m)	0+3×858
36790 (m)	0+1029	38420 (s)	0+2×959+737
36847 (s)	0+1086	38526 (w)	0+2×959+858
		38643 (s)	0+3×959

TABLE II

Ultraviolet absorption spectra of *m*-chlorophenol in the liquid and solid states

Liquid at 32°C		Solid at −180°C	
Wave No. (cm^{-1}) and Intensity	Assignment	Wave No. (cm^{-1}) and Intensity	Assignment
35508 (sbb)	0,0	35564 (sb)	0,0
36447 (sbb)	0 + 939	36485 (sb)	0 + 921
37398 (wb)	0 + 2 × 939	37414 (wbb)	0 + 2 × 921

ground state frequencies observed by Kohlrausch and Pongratz. The upper state frequencies 180 and 225 cm^{-1} correspond probably to the Raman frequencies 193 and 241 cm^{-1}; the observed ground state frequencies 190 and 235 cm^{-1} are also in good agreement with the Raman data. The frequency 120 cm^{-1} may be

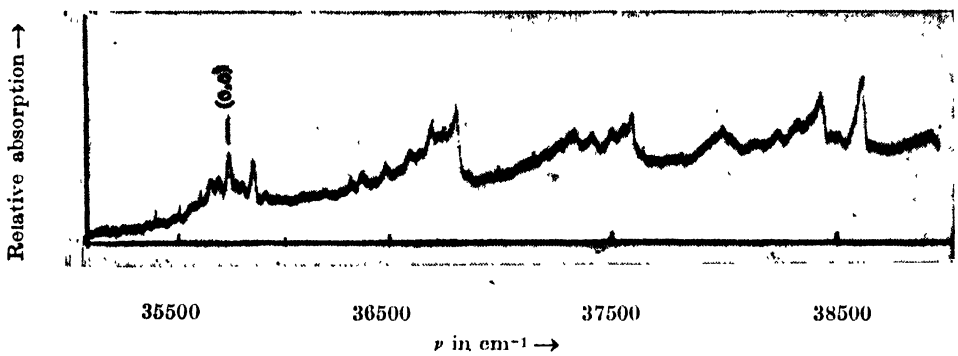

Fig. 1. Microphotometric record of the ultraviolet absorption spectrum of *m*-chlorophenol in the vapour state.

the excited state value of the observed ground state frequency 151 cm^{-1}. Though Kohlrausch *et al.* did not report any Raman shift of this magnitude, we are probably justified in taking 151 cm^{-1} as a fundamental frequency, because such low frequency fundamentals are usually observed in the ultraviolet absorption spectra of phenol compounds (Swamy, 1953; Ramasastry, 1951). This frequency probably represents an out of plane deformation vibration. The other excited state frequencies 362, 503, 612, 737, 858, 959 and 1029 cm^{-1} can be correlated with the ground state frequencies 409, 527, 684, 769, 890, 995 and 1066 cm^{-1} respectively, observed in Raman effect. The strong band at 36847 cm^{-1} may be analysed as 0+1086 cm^{-1}, there being two weak ground state frequencies 1088 and 1157 cm^{-1} reported by Kohlrausch *et al.* Similarly, the weak band at 36988 and 37316 cm^{-1} may be assigned as 0+1227 and 0+1555 cm^{-1} respectively,

since there are two Raman lines at 1253 and 1583 cm^{-1}, but those two bands can also be alternatively assigned as combination frequencies as shown in Table I. The band at 35710 cm^{-1}, on the longer wavelength side of the 0, 0 band at a distance of 51 cm^{-1} and those at 35793 and 35834 cm^{-1} with shifts of 32 and 73 cm^{-1} from the 0, 0 band on the short wavelength side may be explained as $v' \rightarrow v$ transitions as shown in Table I.

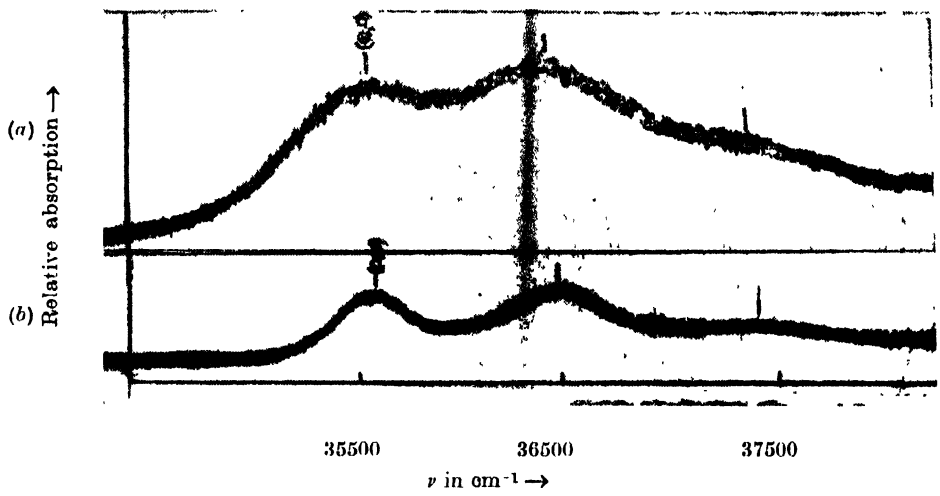

Fig. 2. Microphotometric records of the ultraviolet absorption spectra of *m*-chlorophenol. (*a*) Liquid at 32°C. (*b*) Solid at −180°C.

In the spectrum of the liquid there are three broad bands with centres approximately at 35508, 36447 and 37398 cm^{-1}, the centre of the first band being taken as the position of the 0, 0 band. Thus it is seen that the liquefaction of the vapour results in a shift of about 260 cm^{-1} towards red of the 0, 0 band. The three bands due to the liquid show a constant separation of about 939 cm^{-1}. Comparing this with the frequencies observed in the spectrum of the vapour, it appears that this smaller value may be due to uncertainty in the location of the 0, 0 band exactly in the case of the liquid. The shift of the 0,0 band may be due to association of the molecules through the O—H group.

When the liquid is frozen and cooled to − 180°C there is no appreciable change in the position of the 0, 0 band. The bands are a little sharper but still quite broad. This large width of the bands may be produced by the interaction of the permanent dipoles in the neighbouring molecules with the transition moment of the excited molecule. It is well known that large splittings are observed in some cases of substituted toluenes and dichlorobenzenes (Swamy, 1952, 1953; Sen, 1957). In the present case such splitting may be small and the large width of the individual bands may be responsible for the overlapping of the components and producing only a single broad band in place of its resolved components.

o-Bromoanisole

The absorption spectrum of *o*-bromoanisole in the vapour state consists of about 17 prominent bands. The strongest band on the long wavelength side at 35615 cm^{-1}, which persists at $-20°C$, has been taken as the 0, 0 band. The other bands have been interpreted on the basis of the fundamental frequencies 221, 358, 517, 632, 685, 744, 955, 1031 and 1233 cm^{-1} in the upper state and their combinations, and frequencies 189 cm^{-1} 233 cm^{-1} in the ground state. The acd frequencies 517, 632, 685, 744, 955, 1031 and 1233 cm^{-1} evidently correspond to the ground state frequencies 544, 659, 743, 792, 1023, 1122 and 1237 cm^{-1} observed in the infrared (Lecomte, 1938). No infrared data are available for frequencies lower

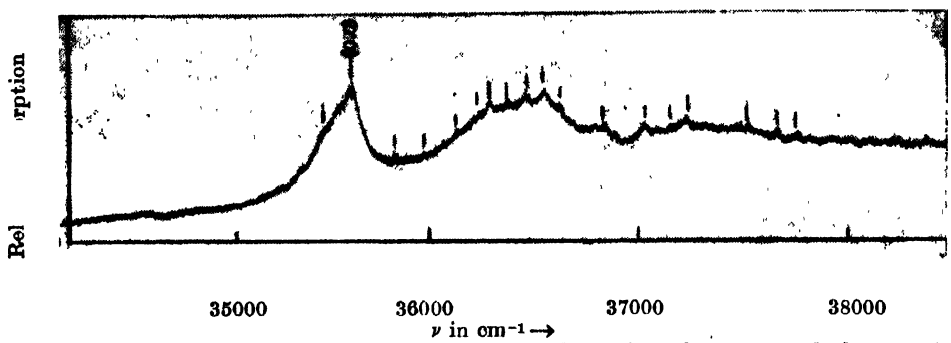

Fig. 3. Microphotometric record of the ultraviolet absorption of spectrum of *o*-bromoanisloe in the vapour state.

than 500 cm^{-1} and the Raman spectrum had not been studied by any previous worker, but the assignment of the frequencies 221 and 358 cm^{-1} to fundamental modes is probably justified. The frequency 358 cm^{-1} represents in all probability in the excited state one of the components of the e^{+}_{g} mode (606 cm^{-1} in the ground state) of the benzene molecule which splits up into two totally symmetric components in the C_s point group. Further, similar band has also been observed in the case of other substituted anisoles (Suryanarayana and Rao, 1956). The frequency 221 cm^{-1} may be correlated to the observed ground state frequency 233 cm^{-1}, which again may represent an out of plane bending mode usually observed in the spectrum of disubstituted benzenes.

In the spectrum of the liquid only four broad bands are observed. Taking 35225 cm^{-1} as the position of the 0, 0 band, the other bands are separated from the 0,0 band by 221, 961 cm^{-1} and the first harmonic of 961 cm^{-1}. Thus it is seen that with the liquefaction of the vapour, the 0, 0 band is shifted by about 390 cm^{-1} towards red.

When the liquid is solidified and cooled to $-180°C$, no further resolution of the bands into components is observed. Taking 35139 cm^{-1} as the position of the 0, 0 band of the system, it is seen that the band system is further shifted towards longer wavelengths by about 86 cm^{-1} with the solidification of the liquid. The other bands of the solid represent excited state frequency 970 cm^{-1},

TABLE III

Ultraviolet sbsorption bands of *o*-bromoanisole in the vapour state

Wave No. (cm^{-1}) and Intensity	Assignment
35382 (w)	0 - 233
35438 (w)	0—189
35615 (vs)	0,0
35836 (w)	0+221
35973 (w)	0+358
36132 (mw)	0+517
36247 (mw)	0+632
36300 (s)	0+685
36359 (mw)	0+744
36468 (ms)	0+632+221
36570 (ms)	0+955
36646 (w)	0+1031
36848 (w)	0+1233
37039 (m)	0+685+744
37192 (w)	0+955+632
37246 (m)	0+955+685
37520 (m)	0+2×955
37620 (w)	0+2×685+632

TABLE IV

Ultraviolet absorption bands of *o*-bromoanisole in the liquid and solid states

Liquid at 32°C		Solid at −180°C	
Wave No. (cm^{-1}) and Intensity	Assignment	Wave No. (cm^{-1}) and Intensity	Assignment
35225 (s)	0,0	35139 (s)	0,0
35496 (w)	0+221		
36186 (s)	0+961	36109 (s)	0+970
37136 (s)	0+2×961	37081 (s)	0+2×970

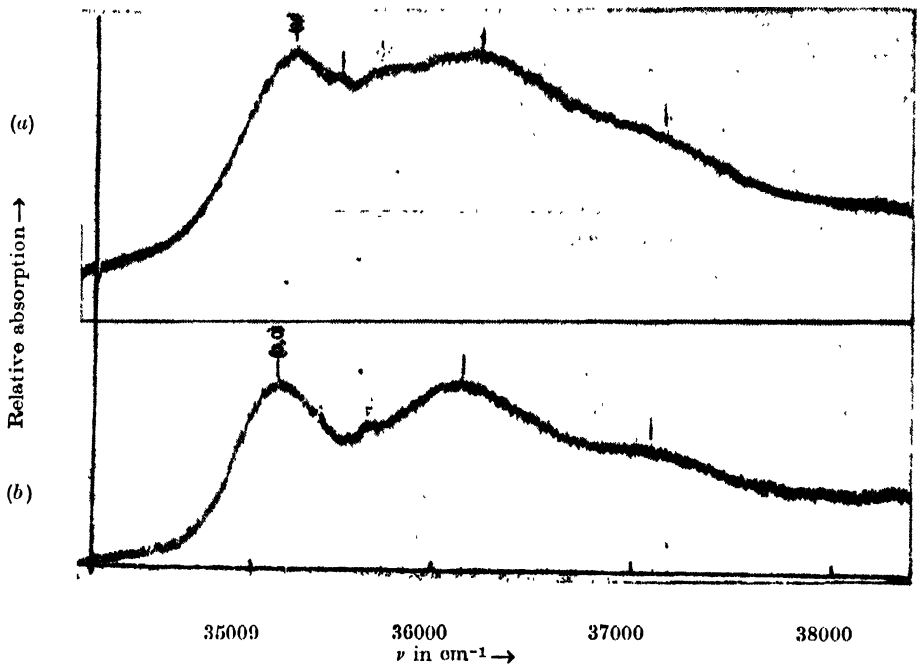

Fig. 4. Microphotometric records of the ultraviolet absorption spectra of *o*-bromoanisole. (a) Liquid at 32°C, (b) Solid at −180°C.

The disappearance of the other bands is due to broadening and consequent overlapping of the bands of the vapour, in the states of aggregation.

The bands are broad in the case of the liquid and the solid states. In the former case, both $v \rightarrow v$ transition and fluctuating intermolecular field may be responsible for the large width. Since both these causes disappear in the solid state, the persistence of the large width of the bands in this case may be due to unresolved components into which each band may have been split up by the interaction of the transition moment and permanent dipole of the surrounding molecules in the lattice.

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